

CATALYZED COAL CONVERSION USING WATER OR ALCOHOLS

Bradley C. Bockrath and Henry M. Davis

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236

Water and some alcohols such as 1-octanol have certain properties that can be used to good advantage in coal liquefaction. The use of water as a liquefaction solvent has been explored in work reported earlier from this center.^{1,2} High conversions of coal were observed when water was used near or above its critical temperature in the presence of a good catalyst and molecular hydrogen.

Certain properties of water near its critical conditions are advantageous in relation to its use as a liquefaction solvent. Some of these have been discussed in a recent review³ and reports.^{4,5} Water near its critical conditions is an excellent solvent for many organic compounds. Liquefaction experiments that used water as a reaction medium and as a means to transport product oils from insoluble coal residues demonstrate clearly that liquefaction products from coal are soluble in water near the critical temperature and somewhat below the critical density.⁵ In addition, it has been reported that water may directly participate in the thermolytic chemistry of many model compounds, a few examples being quinoline,⁷ dibenzylether,⁸ and benzylphenol.⁹ Thus, it seems possible that water might act as both a physical solvent and a reactant when used as a liquefaction solvent.

Other experiments indicate that yields of tetrahydrofuran extracts determined after heating with water in the absence of hydrogen are a strong function of water density and are markedly lower at subcritical densities.⁶

The chemistry of this intriguing system was explored further by making a series of comparisons between water and a number of other solvents with critical temperatures near that of water. The solvents were chosen to cover a range of solvent power and functionality. Alcohols such as 1-octanol and 1,5-pentandiol gave conversions as high as those with water but at markedly lower total pressure.

EXPERIMENTAL

Detailed experimental procedures have been given.¹ In brief, a set of five 42-mL microautoclaves was used. The entire set was immersed into a preheated, fluidized sandbath. Cooling was provided by immersion in a second fluidized sandbath held at room temperature. Thus, five samples were subjected to nearly identical thermal profiles in one experiment. Agitation was provided by a pneumatic shaker to promote mixing.

The coal was an Illinois No. 6 (River King Mine) bituminous coal. The elemental analysis was C, 73.7%; H, 5.6%; N, 1.5%; O, 14.8%; and S, 4.5%, on a daf basis. The moisture-free ash content was 13.6%. Liquefaction solvents other than water were reagent-grade chemicals used without further purification. Ammonium paramolybdate was added either directly as a dry powder or as an aqueous solution to make 1000 ppm Mo on daf coal. Coal charge was 4.0 g (3.4 g daf) unless otherwise noted. A pressure of 1200 psig hydrogen was applied in all cases before heating. The liquefaction temperature was always 385°C. The critical temperature of water is 374.2°C.

The liquefaction products were recovered using tetrahydrofuran (THF) after pressure letdown. Conversions were determined using room-temperature extraction with

THF. Soluble portions were decanted from residues after centrifugation. Extractions were continued until the supernatant was nearly colorless. Conversion values were based on dry THF-insoluble residue. The reproducibility was usually within $\pm 2\%$.

RESULTS AND DISCUSSION

Previous work has shown that conversions obtained under hydrogen pressure in the presence of water are substantially higher than in its absence.¹ An increase in conversion was found both with and without added catalyst. The effectiveness of water must certainly rest in part on its ability to function as a physical solvent. Density is a key variable governing the solvent strength of water above the critical temperature. To probe the effect of water density on coal conversion, three sets of experiments were carried out. In one, the loading of coal was held constant, and the amount of added water was varied. Conversions measured as a function of time are shown in Figure 1. A second set of experiments was carried out with the ratio of water to coal held constant, but the total amount of both was varied (Figure 2). Finally, the water density was held constant, but the mass of coal was varied (Figure 3).

As may be seen, coal conversion approaches a plateau after reaction for 60 min at 385°C. Conversion is a strong function of water density over the range studied here. The maximum density used, 0.09 g/mL, is considerably below the density at the critical point, 0.315 g/mL. The density used in these experiments was limited by consideration of the total pressure in the autoclave at temperature. At the highest density, the total pressure was estimated to be 5300 psi, with 2600 psi due to hydrogen and 2700 psi due to water.

In the first set of experiments, both the water density and the relative amount of water to coal was varied. The data from the second set of experiments shown in Figure 2 indicate that the spread of conversion values as a function of water density is smaller if the water-to-coal ratio is held constant at 0.85. Nonetheless, water density remains an important determinant of coal conversion even when the relative amount of coal loading is removed as a variable.

Finally, if the amount of coal is increased while the water density is held constant at 0.09 g/mL, the conversion is decreased (Figure 3). Thus, taking the data together, both the water density and the relative amount of coal charged are important determinants of conversion. Conversion is favored by increasing water density and disfavored by increasing coal loading. Increasing density would improve the ability of water to dissolve coal conversion products. Increasing coal loading would increase the probability of retrogressive recombination reactions. The observed trends in conversion can be rationalized on the basis of the relative rate of retrogressive reactions, lower rates being favored by higher water densities and lower coal loadings.

Comparison was made between water and 1,2,4-trimethylbenzene (critical temperature = 378°C est.) to reveal whether it held unusual properties for liquefaction. In this comparison, conversions were measured after heating for 30 minutes at 385°C over the entire composition range of the binary mixtures from pure trimethylbenzene to pure water. The density of total amount of added solvents was always 0.09 g/mL.

The data contained in Figure 4 indicate that water is far superior to trimethylbenzene. In view of the success of toluene as a supercritical solvent for coal,¹⁰ trimethylbenzene might be expected to be a reasonably good liquefaction medium. The performance of water is all the more surprising by comparison.

Water contains hydroxyl groups that trimethylbenzene does not. Figure 4 also includes results obtained with two other hydroxyl-containing compounds, 1-octanol

(critical temperature = 385.5°C) and 1,5-pentanediol (critical temperature = 410°C est.). In binary mixtures with trimethylbenzene, these two alcohols are roughly as, or possibly more, effective than water. However, the alcohols would exert far less pressure than water at the same temperature.

The same data shown in Figure 4 are replotted in Figure 5 on the basis of the molar density of hydroxyl groups, that is, the mols of hydroxyl groups per liter of reactor space. The conversion values increase with hydroxyl density at markedly different rates. Thus, conversion does not depend simply on the total density of hydroxyl groups. This observation favors an interpretation on the basis of bulk solvent and/or diffusional effects rather than direct chemical participation of the hydroxyl group. However, further work is necessary to fully dissect the chemistry.

This preliminary work has shown that certain alcohols and water are effective liquefaction media at 385°C, a temperature near their critical temperatures. Solvency or diffusional effects seem to be the important variables governing conversion, although chemical effects cannot be entirely ruled out. The higher boiling alcohols, 1-octanol and 1,5-pentanediol, are as effective as water, yet their partial pressure for a given density is far lower than that of water.

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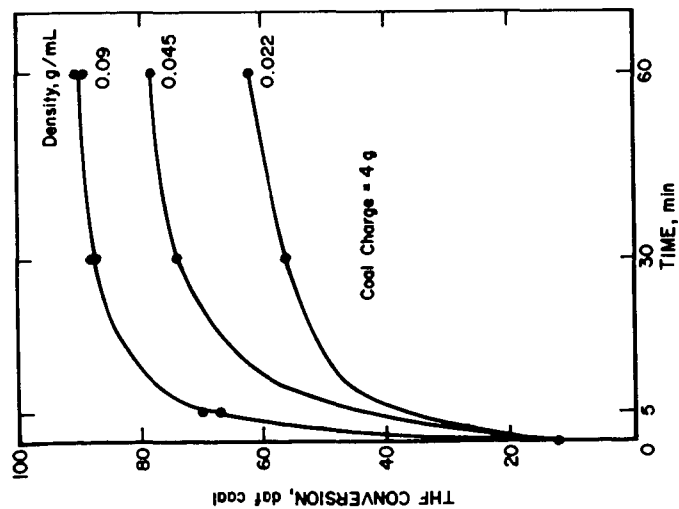


Fig. 1. Conversion and Water Density.

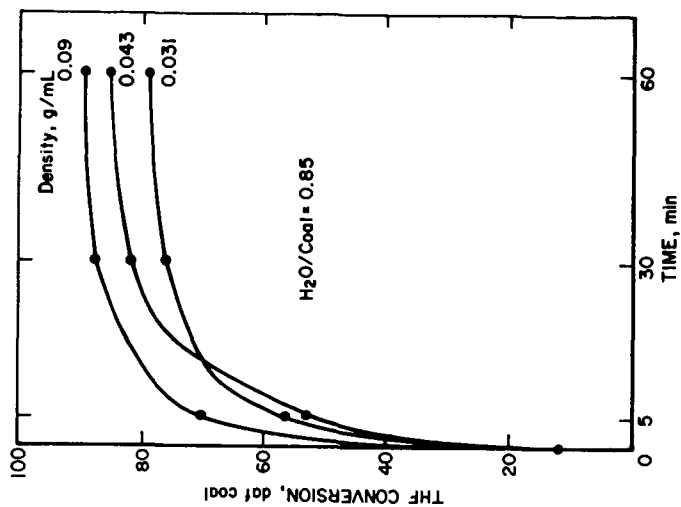
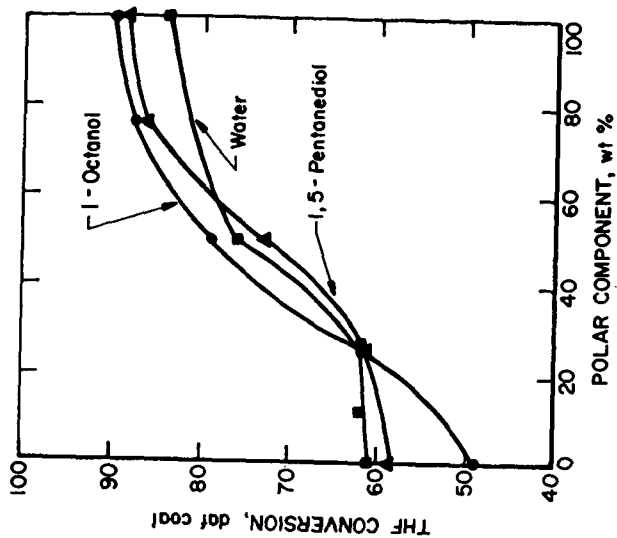
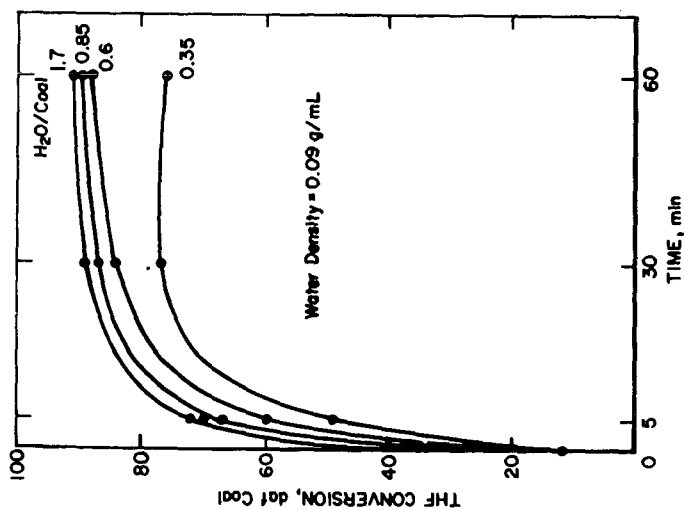


Fig. 2. Conversion and Water Density.



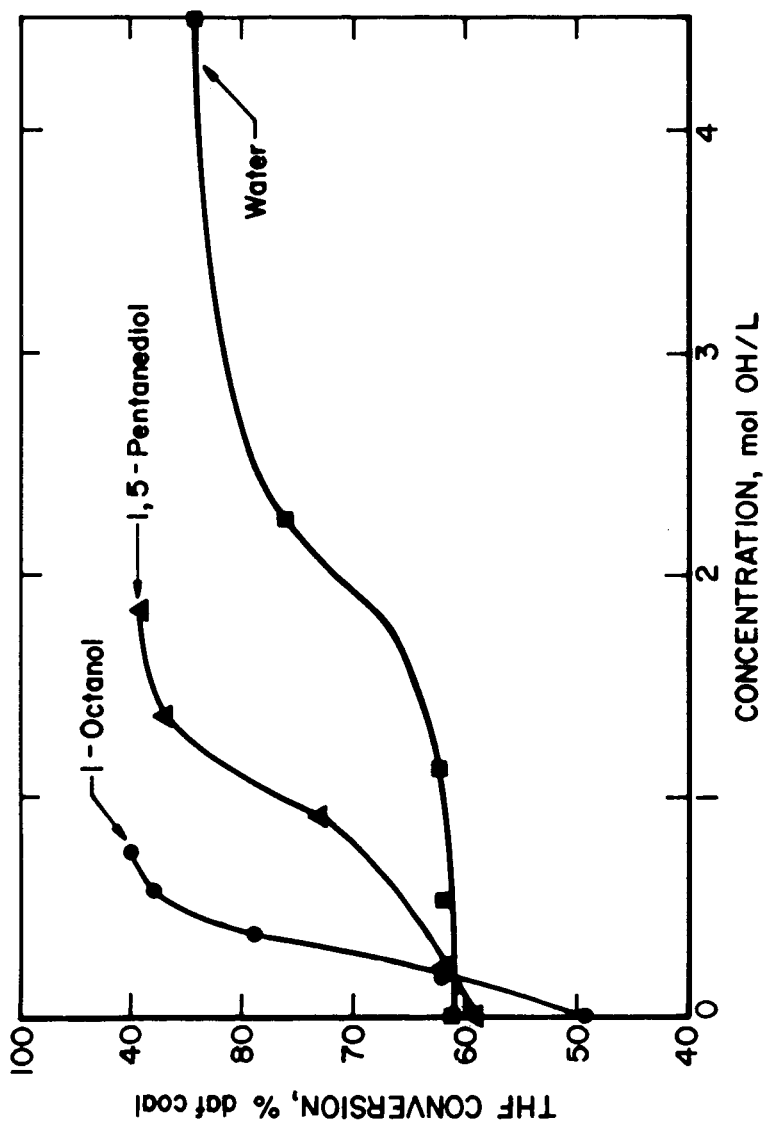


Fig. 5. Conversion in 1,2,4-Trimethylbenzene